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# Long-term decrease in the global atmospheric burden of tetrachloroethene ($C_2Cl_4$)

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[1] We present a 14-year record of tropospheric tetrachloroethene ($C_2Cl_4$) mixing ratios measured each season at remote surface locations throughout the Pacific Basin (71°N–47°S). Our calculated annual mean $C_2Cl_4$ mixing ratio for the extra-tropical northern hemisphere (NH) was 13.9 ± 0.5 pptv in 1989, but declined to less than half this value (to 6.5 ± 0.2 pptv) by 2002. Mid-latitude southern hemisphere (SH) mixing ratios, which were much smaller than NH values, showed interannual variations comparable to measured long-term changes, and the SH annual mean was slightly less in 2002 than in 1989. Driven by the relatively large decrease in NH values, the global $C_2Cl_4$ mixing ratio declined from 6.3 ± 0.6 pptv in 1989 to 3.5 ± 0.2 pptv in 2002. These values suggest that the global $C_2Cl_4$ burden decreased by roughly 205 Gg between 1989–2002, which is consistent with industrial estimates of declining NH emissions over a similar period. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry. **Citation:** Simpson, I. J., S. Meinardi, N. J. Blake, F. S. Rowland, and D. R. Blake (2004), Long-term decrease in the global atmospheric burden of tetrachloroethene ($C_2Cl_4$), *Geophys. Res. Lett.*, *31*, L08108, doi:10.1029/2003GL019351.

## 1. Introduction

[2] Tetrachloroethene ($C_2Cl_4$) is primarily used as a dry cleaning solvent and degreasing agent, and the dominance of its anthropogenic production source makes it a useful tracer for urban/industrial activities [*Atlas et al.*, 1992; *Blake et al.*, 2001, 2003a]. Reaction with OH is the primary $C_2Cl_4$ sink. The atmospheric lifetime of $C_2Cl_4$ [3.5–4 mo; *Singh et al.*, 1996; *Olaguer*, 2002] is shorter than the interhemispheric mixing time [~1 yr; *Seinfeld and Pandis*, 1998] and $C_2Cl_4$ consistently shows a strong interhemispheric gradient, with higher mixing ratios in the northern hemisphere (NH) than in the southern hemisphere (SH) [*Wang et al.*, 1995; *Rudolph et al.*, 1996].

[3] $C_2Cl_4$ was declared a hazardous air pollutant under the U.S. Clean Air Act Amendments of 1990 because of potential health and environmental impacts [*Kleiman and Prinn*, 2000 and references therein]. Recent studies cite decreases in its atmospheric concentration and variability [*Hurst et al.*, 1998; *CMDL*, 2001; *Blake et al.*, 2003a] and industrial emissions [*McCulloch et al.*, 1999; *Kleiman and Prinn*, 2000]. Voluntary reductions of industrial $C_2Cl_4$ emissions began in the U.S. in 1991, and increased solvent recycling and lower production rates of CFC-113, the principal derivative of $C_2Cl_4$, also likely contributed to the measured $C_2Cl_4$ decreases. Here we present the longest continuous record of the global $C_2Cl_4$ mixing ratio, and we discuss $C_2Cl_4$ emission and growth rate trends between 1989–2002.

## 2. Experimental

[4] Our group has measured global $C_2Cl_4$ mixing ratios since Dec 1988 as part of a long-term program that monitors other trace gases [*Mayer et al.*, 1982; *Blake and Rowland*, 1986; *Wang et al.*, 1995; *Gupta et al.*, 1998; *Simpson et al.*, 2002]. Each season (Mar, Jun, Sep and Dec), a total of 50–80 whole air samples are collected over a 3-week period at 40–45 remote surface locations in the Pacific Basin. Samples were taken less frequently in 1991 and 1992 (Apr, Aug and Dec) because of political events, and our 14-year data set (Dec 1988–Dec 2002) is missing three seasons of $C_2Cl_4$ data from early in our program (Sep 1990, Mar–Jun 1993). The sampling network extends from 71°N to 47°S and includes Alaska; the west coasts of USA and Mexico; small central and south Pacific islands; and New Zealand (see www.physsci.uci.edu/~rowlandblake/samplinglocationsmap.html). Each sample is collected over 1 minute into a conditioned, evacuated 2-L stainless steel canister equipped with a bellows valve, typically along the coast when the wind is from the ocean.

[5] Three aliquots from each sample are analyzed for halocarbons at our UCI laboratory, using two GC/ECDs (HP-6890) and one GC/MSD (HP-5793) [see *Blake et al.*, 2003a for details]. The results from each aliquot are averaged to give one $C_2Cl_4$ mixing ratio for each sample. Our $C_2Cl_4$ calibration scale dates back to 1988 and is regularly updated by preparing new primary standards [*Wang et al.*, 1995; *Colman et al.*, 2001]. Since 1996 we have also performed regular intercomparisons with NCAR to ensure that our calibration has not drifted. The $C_2Cl_4$ precision in 1989 was 3% or 0.1 pptv, whichever was larger, and is currently 1% or 0.05 pptv. Informal calibration tests show that UCI $C_2Cl_4$ mixing ratios are about 5% higher than NCAR values at levels of 10 pptv. Our accuracy is 8% at 2 pptv and 3% at 40 pptv, and the $C_2Cl_4$ detection limit is now 0.05 pptv.

[6] *Dimmer et al.* [2001] discuss difficulties in defining remote sites for background tropospheric halocarbon mea-


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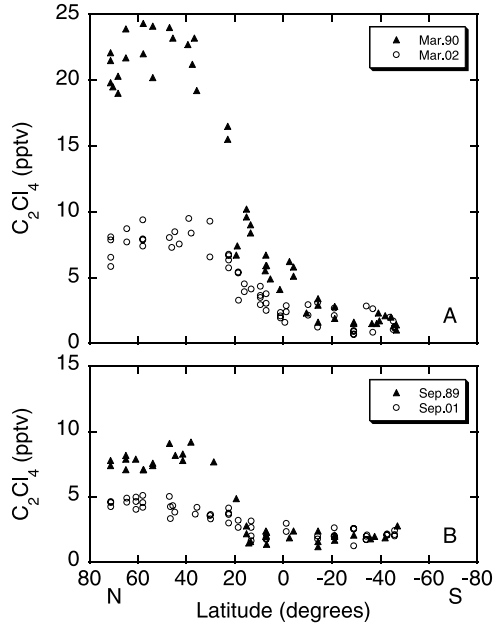


**Figure 1.** Latitudinal distribution of $C_2Cl_4$ at surface sites in the Pacific Basin (a) Mar 1990, 2002; (b) Sep 1989, 2001.

surements because of local contamination. Here each $C_2Cl_4$ data point was inspected and those likely contaminated from local sources were removed (typically 1–5 samples per season). A second issue is the use of Pacific Basin measurements as a global surrogate. The concept of 'background' does not apply very well to $C_2Cl_4$ because it is short-lived relative to global mixing times and, unlike longer-lived compounds such as $CH_4$, $C_2Cl_4$ mixing ratios decrease between 'remote' and 'very remote' sampling locations and show a fairly wide spread of atmospheric variability. Here we note that our sampling locations are remote but show more continental $C_2Cl_4$ influence than the CMDL network (Section 3.3).

[7] For each season, global surface $C_2Cl_4$ mixing ratios were determined by separating the Earth into 16 latitudinal bands or 'boxes' containing roughly equal volumes of tropospheric air (the boundaries lie at the equator and 7.2, 14.5, 22.0, 30.0, 38.7, 48.6 and 61.0° in each hemisphere). Boxes where no data were collected (south of 48.6°S) were assigned extrapolated values and errors using data from neighbouring boxes ($C_2Cl_4$ is fairly well-mixed in the SH, Figures 1a and 1b; though see discussion in Section 3.3). Each global seasonal $C_2Cl_4$ mixing ratio is the mean of the 16 box averages. The uncertainty in each box average is the standard error, SE. The global seasonal mean uncertainty is the sum of SEs for each box, added in quadrature, divided by the number of boxes. The global annual mean uncertainty is the sum of SEs for each season added in quadrature.

## 3. Results and Discussion

### 3.1. Latitudinal Distribution

[8] The measured $C_2Cl_4$ mixing ratios are higher in the NH than SH (Figure 1). Consistent with this, most industrial usage and therefore emission of $C_2Cl_4$ takes place in the NH, with much lower usage and emission in the SH [*McCulloch et al.*, 1999]. High-latitude NH $C_2Cl_4$ mixing ratios were 20–25 pptv in Mar 1990 compared to 5–10 pptv in Mar 2002 (Figure 1a), clearly illustrating that NH $C_2Cl_4$ levels have decreased significantly over the past decade or so.

[9] The overall low $C_2Cl_4$ mixing ratios in the SH and lack of $C_2Cl_4$ 'hot spots' in the equatorial and south Pacific suggest that oceanic sources of $C_2Cl_4$ [*Singh et al.*, 1996; *Khalil et al.*, 1999] play a relatively minor role, if any, in the $C_2Cl_4$ budget. During airborne missions over the Pacific our group has consistently noted a lack of evidence for oceanic $C_2Cl_4$ emissions, even in areas where other oceanic species such as $CHBr_3$, $CH_3I$, DMS, and/or light alkyl nitrates are strongly elevated [e.g., *Blake et al.*, 2003b]. Therefore we suggest that most SH $C_2Cl_4$ originates from industrial emissions, either directly into the SH troposphere or transported from the NH.

### 3.2. Seasonal Cycle

[10] Seasonal $C_2Cl_4$ means were calculated in each hemisphere by averaging the four high-latitude NH boxes (30–90°N, chosen to avoid the steep transition from NH to SH mixing ratios at tropical NH latitudes) and the four most southerly boxes in which we sample (14.5–48.6°S). $C_2Cl_4$ shows clear, anticorrelated seasonal signals in each hemisphere, with a much larger amplitude in the NH than SH (Figure 2). Maximum (minimum) $C_2Cl_4$ mixing ratios occur in late winter (summer) in each hemisphere, as verified in the SH using samples collected weekly at Norfolk Island (29°S) since 2001. Industrial $C_2Cl_4$ emissions likely are not seasonal [*McCulloch and Midgley*, 1996], and the summer $C_2Cl_4$ minimum is caused by the summer OH maximum in each hemisphere [*Spivakovsky et al.*, 2000]. Though $C_2Cl_4$ reacts relatively quickly with chlorine radicals, Cl is not a significant $C_2Cl_4$ sink because average tropospheric Cl levels are typically low [*Rudolph et al.*, 1996; *Singh et al.*, 1996]. Further, the lifetime of $C_2Cl_4$ with marine boundary layer (MBL) Cl is much longer than the mixing time between the MBL and free troposphere [*Wingenter et al.*, 1996]. Driven by the relatively high $C_2Cl_4$ levels in the

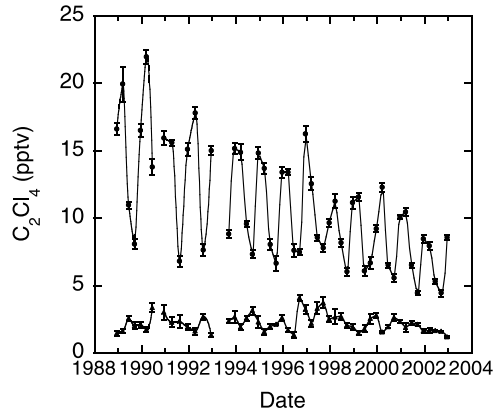


**Figure 2.** Seasonal $C_2Cl_4$ mixing ratios in the high NH (30–90°N; circles) and mid-latitude SH (14–49°S; triangles). Curve fits are interpolated (pass through each point); gaps show missing seasons; error bars are described in the text.

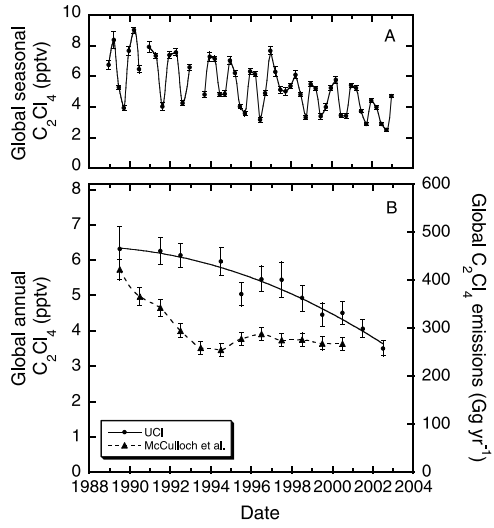


**Figure 3.** (a) Global seasonal $C_2Cl_4$ mixing ratios from Dec 1988–Dec 2002; (b) Global annual $C_2Cl_4$ mixing ratios (UCI) and industrial emission estimates [*McCulloch et al.*, 1999; *A. McCulloch*, personal communication, 2003]. In Figure 3b the two y-axes are aligned as described in Section 3.5. Curve fits are interpolated (seasonal and industrial data) and second-order polynomial (annual data); gaps show missing seasons; error bars are described in the text.

NH and its strong seasonal cycle, the global $C_2Cl_4$ burden also peaks in late winter (Figure 3a).

### 3.3. Literature Comparison

[11] For overlapping sampling periods (Sep 1989–Jun 1990), the global $C_2Cl_4$ mixing ratio from our network (7.3 pptv; *Wang et al.*, 1995) agrees well with that of *Rudolph et al.* [1996] (8.4 pptv) to within the stated uncertainties. During an April–May 1998 cruise in the northeast Atlantic (20–63°N; 20°W), *Dimmer et al.* [2001] observed lower $C_2Cl_4$ mixing ratios for air masses originating over the open ocean (4.3 ± 0.8 pptv) than for those transported from northern Europe (9.7 ± 2.6 pptv). Our mean $C_2Cl_4$ mixing ratio at comparable latitudes during a similar time period (the average of Mar and Jun, 1998) was 9.0 ± 2.4 pptv. Calibration tests between the two laboratories show $C_2Cl_4$ agreement to within 10%, and the similarity of our results to their Europe-influenced (rather than open ocean) average suggests a comparable continental influence on our eastern Pacific samples. During airborne missions we have measured moderately elevated (by 2–4 pptv) $C_2Cl_4$ mixing ratios at low altitude over the eastern Pacific as a result of trans-Pacific Asian pollution [*Blake et al.*, 2001, 2003a]. We suggest that Asian outflow has a low-level, pervasive influence on $C_2Cl_4$ mixing ratios over the eastern Pacific. By contrast, local contamination from North America likely causes the few $C_2Cl_4$ outliers observed in the NH during most of our sampling trips.

[12] Annual global $C_2Cl_4$ mixing ratios from the NOAA/CMDL network, which are available from 1995–2002 (CMDL-2003 scale), are lower than UCI estimates by 1.5–2.7 pptv (factors of 1.7–2.1) [*CMDL*, 2001; *S. Montzka*, personal communication, 2003]. This disparity lies outside the reported accuracy of each group and we believe it is primarily explained by sampling location differences. While the global mean from CMDL was calculated from a smaller number of very remote locations (Alert, Barrow, Niwot Ridge, Mauna Loa, Kumukahi, Samoa, Cape Grim, and South Pole), our measurements are likely more influenced by low-level continental emissions, as discussed above for the NH. In the SH this is consistent with our Dec 1995 New Zealand $C_2Cl_4$ data, which are 1–1.5 pptv higher than MBL aircraft data collected at the same time but south of New Zealand in a more remote region (to 60°S) [*Blake et al.*, 1999].

[13] The actual amount of $C_2Cl_4$ in the atmosphere at any time includes mixing ratios in urban, rural, remote and very remote locations. Because much industrially-emitted $C_2Cl_4$ decays during transport to very remote locations, measurements made in such locations will underestimate instantaneous global $C_2Cl_4$ levels. We suggest that our measurements consistently represent 'remote' rather than 'very remote' mixing ratios.

### 3.4. Mixing Ratio Trends

[14] The annual global $C_2Cl_4$ mixing ratio inferred from our measurements nearly halved during the measurement period, from 6.3 ± 0.6 pptv in 1989 to 3.5 ± 0.2 pptv in 2002 (Figure 3b). The $C_2Cl_4$ decline was not linear but increased from about 0.1 pptv yr$^{-1}$ in 1990 to 0.4 pptv yr$^{-1}$ in 2002. $C_2Cl_4$ mixing ratios in the high-latitude NH (30–90°N) decreased from 13.9 ± 0.5 pptv in 1989 to 6.6 ± 0.3 pptv in 2002, indicating that the global decrease was primarily driven by changes in the NH (Figure 2). The interhemispheric ratio of $C_2Cl_4$ (high-latitude NH values ÷ mid-latitude SH values) declined from 7.1 ± 0.6 in 1989 to 4.5 ± 0.3 in 2002. The peak-to-trough amplitude of the global $C_2Cl_4$ seasonal signal also decreased in the 1990s, from 4–5 pptv in 1989–90 to 1.5–2 pptv in 2001–02 (Figure 3a). Between 1995–2002 the UCI data show a 30% decrease in annual global $C_2Cl_4$ mixing ratios (Figure 3b), and by comparison the data from CMDL show a 25% decrease over this same period [*S. Montzka*, personal communication, 2003].

[15] In the mid-latitude SH, the annual $C_2Cl_4$ mixing ratio was 2.1 ± 0.2 pptv in 1989; remained fairly constant between 1989–95; notably increased in mid-1996; then declined by roughly a factor of two from 2.9 ± 0.2 pptv in 1997 to 1.5 ± 0.1 pptv in 2002. A $C_2Cl_4$ increase beginning in late-1996 is also evident in the NH (Figure 2). Interestingly, the $C_2Cl_4$ increase in both hemispheres occurred shortly after the Montreal Protocol ban on CFCs, which became effective in many countries on Jan 1, 1996. It is likely that some of the CFC solvent usage banned under the Protocol temporarily shifted to non-protocol solvents such as $C_2Cl_4$ in both hemispheres, shortly after the prohibition took effect.

### 3.5. Global Emissions

[16] Using a single box model calculation, a global $C_2Cl_4$ lifetime of 4 months, and accounting for a mean, 10% decrease in $C_2Cl_4$ mixing ratios with height in the troposphere [see *Wang et al.*, 1995], the global $C_2Cl_4$ mixing ratios in 1989, 2000 and 2002 correspond to annual emissions of 465 ± 45, 330 ± 20, and 260 ± 15 Gg yr$^{-1}$, respectively (Figure 3b). Global industrial $C_2Cl_4$ emission

estimates (based on audited sales data) are available until 2000 and were 423 ± 21 in 1989 and 268 ± 13 Gg $yr^{-1}$ in 2000 [*McCulloch et al.*, 1999; *A. McCulloch*, personal communication, 2003]. Though the 42–62 Gg $yr^{-1}$ offset between the UCI and *McCulloch et al.* estimates may be related to a combination of uncertainty and our network's proximity to $C_2Cl_4$ source regions (Section 3.3), which requires a systematic offset of only 0.75 pptv to give an additional emission of ~55 Gg $yr^{-1}$, our emission calculation does not account for longitudinal spatial gradients in $C_2Cl_4$ or OH, and we cannot draw this conclusion with certainty.

[17] Because we sample in the same narrow range of longitudes (per latitude band) each season, our measurements are suitable for year-to-year trend analysis. Our annual mixing ratios suggest a global $C_2Cl_4$ burden decrease of ~135 Gg between 1989–2000 and 205 Gg between 1989–2002. The former estimate is consistent with the ~155 Gg global industrial emission decline for 1989–2000. However the pattern of this decrease differs between UCI and *McCulloch et al*. Whereas the UCI $C_2Cl_4$ burden decreases at an increasing rate, the industrial estimates sharply decrease between 1989–94 then stabilize between 1995–2000 (Figure 3b). The UCI measurements and *McCulloch et al.* estimates are each internally consistent, and the reason for this difference is unclear. It is unlikely that meteorology contributes to long-term trends in global growth rates [*Warwick et al.*, 2002] or that variations in global OH levels caused the difference [*Krol et al.*, 2003]. Together with A. McCulloch (University of Bristol) we investigated whether unreported/changing $C_2Cl_4$ production in the 1990s could have caused the discrepancy. Though we found there has been a major shift of $C_2Cl_4$ emissions from Japan to industrial regions of China (mostly in the northeast) in the past decade, their combined emissions have stayed fairly constant at around 45 Gg $yr^{-1}$. Instead, global $C_2Cl_4$ emission reductions have been driven mainly by North America and Europe. It also appears unlikely that the global distribution of $C_2Cl_4$ emissions has shifted latitudinally so as to significantly affect $C_2Cl_4$ mixing ratio trends based on latitudinal gradients in OH. We speculate that the slower decline in observed $C_2Cl_4$ mixing ratios compared to industrial emission estimates is related to a slower than anticipated introduction of technology to reduce industrial $C_2Cl_4$ leakage/emissions.

## 4. Conclusions

[18] The global $C_2Cl_4$ burden shows a long-term decrease over the 14-year period 1989–2002, declining more rapidly from 0.1 pptv $yr^{-1}$ in 1990 to 0.4 pptv $yr^{-1}$ in 2002. The global decline is driven by reduced industrial emissions primarily from North America and Europe. A small $C_2Cl_4$ increase in each hemisphere in 1996 likely resulted from increased $C_2Cl_4$ usage immediately following the first phase of the Montreal Protocol. Our measurements and industrial emission estimates suggest a total $C_2Cl_4$ burden decrease of 135–155 Gg between 1989–2000. However the pattern of $C_2Cl_4$ decline differs between the two estimates, possibly related to a slow introduction of technology to reduce $C_2Cl_4$ release into the atmosphere.

[19] Comparisons with other studies highlight the variability of $C_2Cl_4$ mixing ratios depending on proximity to local sources, and show the pervasive, low-level influence of Asian outflow on $C_2Cl_4$ values over the eastern Pacific. By contrast, our observations suggest that an oceanic source of $C_2Cl_4$, if present, is relatively minor.

[20] **Acknowledgments.** We dedicate this work to Murray McEachern, whose outstanding logistical and interpersonal skills have been central to this project's success. We thank our group members for sample collection and analysis, Archie McCulloch (Univ. of Bristol) and Stephen Montzka (NOAA/CMDL) for valuable discussions and for sharing unpublished data, and Oliver Wingenter for helpful discussions. The project is funded by NASA contract NAGW-452.

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